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## Thermoreversible cross-linking of rubber

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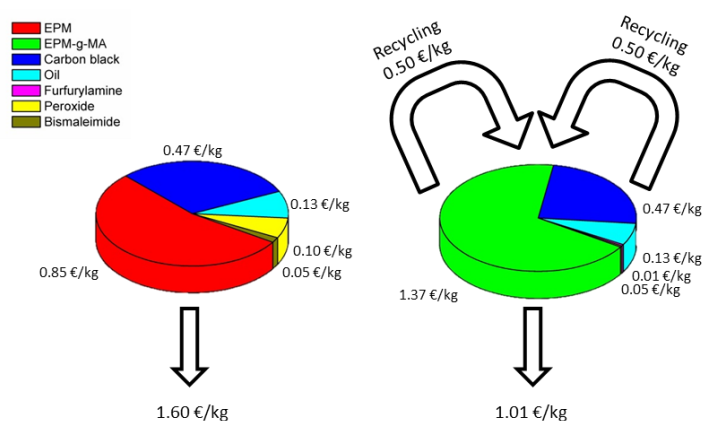
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# Chapter 9

## Technology Assessment

Currently, used rubber products cannot be reprocessed after their product life due to the irreversible methods traditionally applied for cross-linking. Thermoreversible cross-linking provides a new approach and allows for the development of recyclable rubber products. This development also advances the state of technology with respect to the recycling of rubber compounds with retention of material properties. The current process for the production of peroxide cured EPM rubber compounds does not have to be significantly adapted to facilitate the production and recycling of these new, reprocessable rubber compounds. Being able to recycle the new material twice without any significant loss of material properties more than compensates for the higher costs of the raw materials required for their production. The production and recycling was found to be economically feasible as it is estimated to be 33% lower than the production of conventional, peroxide cured EPM compounds. Unfortunately, the applicability of the new, reprocessable rubber is limited to room temperature applications due to the rapid deterioration of the material properties at elevated temperatures with respect to irreversibly cross-linked rubbers. Several alternatives are proposed to overcome issues regarding the temperature stability of the reprocessable rubber. Finally, the reinforcing effect of short cut aramid fibers on the material properties of the newly developed thermoreversibly cross-linked EPM rubbers is studied.



This chapter is based on: L. M. Polgar, E. de Ruiter, M. van Duin and F. Picchioni. 'The application of thermoreversibly cross-linked rubber products' *Submitted to Polymers-Plastics Technology and Engineering Journal (Taylor and Francis)* **2016**

## 9.1. Introduction

The final step in investigating the production, recycling and applicability of the newly developed, fully reprocessable rubber compounds is a technology assessment. This relies on the comparison with respect to conventional, peroxide cured EPM rubber compounds with similar material properties. These are intrinsically not processable after cross-linking. The technical assessment takes into consideration aspects related to the current production process of rubber products, which may have to be revised in order to implement the production and recycling of the reprocessable material. Secondly, the production of recyclable rubber materials is only economically viable if the benefits of producing them outweigh the extra costs for their production. The collection of recyclables should also be taken into consideration in this analysis. Finally, the conditions at which products containing the newly developed reprocessable rubber compounds can be applied, with a focus on the temperature stability, are further investigated. Here, the newly developed thermoreversibly cross-linked rubbers are compared with conventional, peroxide cured and sulphur vulcanized EPM rubber compounds with similar material properties (at room temperature) which are intrinsically not processable after cross-linking. Some alternative DA diene-dienophile couples are studied and suggested for further research in order to overcome any shortcomings of the material at hand. Finally, the material properties of the fiber-filled rubber compounds with the newly developed thermoreversibly cross-linked EPM rubber is compared with a fiber-filled, peroxide cured EPDM.

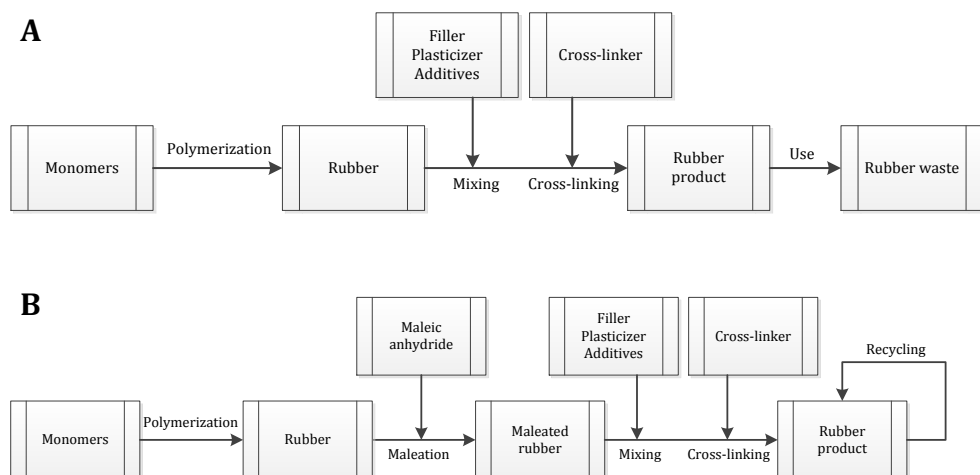
## 9.2. Production Process

Currently, the production process of rubber products consists of a mixing stage and a subsequent molding step, e.g. compression, extrusion or injection molding, to shape and cure the final product. The rubber compound can be mixed in batches or continuously. Although continuous processing is generally preferred, an ongoing discussion regarding the use these both processes for the production of traditional rubbers evokes some of their advantages and disadvantages (Table 9.1) [1]. The main differences in production costs are related to staffing requirements, machinery and installation costs. Batch mixers are generally more easily adaptable by adjusting process variables such as temperature, rotational speed and mixing time. In a continuous process, the shear rate, temperature and residence time can be adjusted. The main disadvantage of continuous mixing is the need for homogeneous and easily processable materials. In any case, the uniformity of the rubber compound must always be consistent.

**Table 9.1.** *Advantages and disadvantages of producing rubbers by batch and continuous mixing.*

	<b>Advantages</b>	<b>Disadvantages</b>
<b>Batch mixing</b>	Handling of irregular materials Little or no preparation of materials Robust machinery that lasts long.	Inefficient use of energy Batch to batch variations. Labor intensive.
<b>Continuous mixing</b>	Steady energy consumption. Little operator attendance required. Uniform output. Short residence times	Not cost effective for short runs. Requires special machine configurations. Unable to process irregular materials. Requires automatic controls.

The production of the rubber compounds is examined for a business-to-business case in which the materials are sold to a company that remolds them into the desired products. The following analysis must be considered as a preliminary case study with no pretence of being exhaustive nor accurate. It just serves the aim of illustrating, in broad strokes, the major effects to be considered for an economic comparison. The production of the conventional, peroxide cured rubber compounds is chosen as a reference because it also allows for the cross-linking of saturated elastomers such as EPM. The peroxide curing process is simplified to a process in which pre-mixed additives are added to the homogenized gum rubber in a batch mixer before adding the peroxide cross-linkers (Figure 9.1A). It must be noted that the temperature of the batch mixer must be kept relatively low (typically below 120 °C) to prevent premature decomposition of the peroxides during mixing. The choice for a batch mixer to compare the two production processes is based on several reasons. First of all, the used, reprocessable rubber products are expected to have more irregular shapes due to wear and tear during use and are therefore more easily reprocessed on a batch mixer. Furthermore, preliminary experiments showed that relatively long residence times ( $\pm 10$  min) are required for the proper mixing and de-cross-linking of the reprocessable rubber compounds. Although the extrapolation of these residence times from a batch process to an extruder set-up is not straightforward, it is expected that relatively long residence times are still required to achieve complete de-cross-linking via the retro-Diels-Alder reaction. Meanwhile continuous mixing is not viable for residence times of longer than 20 to 30 s [1]. The production of the reprocessable EPM rubber compounds requires an additional modification step with furfurylamine (FFA) and the addition of a bismaleimide (BM) instead of a peroxide cross-linker (Figure 9.1B). Here, the temperature in the mixer must be kept relatively high to prevent premature cross-linking during mixing and subsequent degradation due to the high shear forces applied to the material.



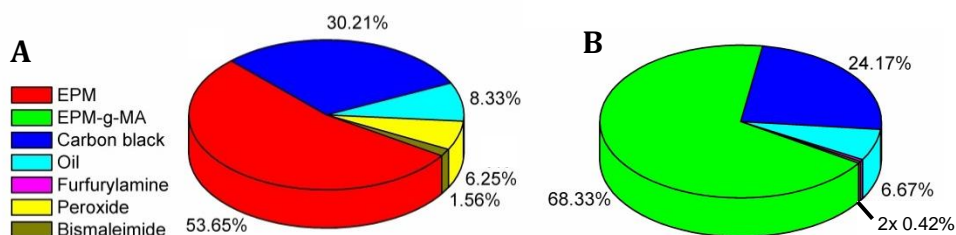
**Figure 9.1.** Schematic production process of A: conventional, peroxide cured and B: reprocessable rubber compounds.

The extra modification step that is required for the production of the reprocessable rubber compounds does not significantly affect the processing times and does not necessarily require any extra equipment. The same is true for the reprocessing of used material. Unfortunately, the use of the chemicals required for the production of the new, reprocessable rubber compound (FFA and BM) does require a revision of the current machinery to minimize the safety and health risks that accompany their use. Since FFA is harmful by oral and skin contact, the installation of an injection system into the pressure lid of the batch mixer is required. BMs are even more toxic chemicals that are lethal by inhalation and can cause severe eye damage and irritation to the skin. Although the BM will most probably be completely absorbed in the rubber compound, the installation of a ventilation system may still be required.

### 9.3. Economic feasibility

An economic feasibility study considers all adjustments that have to be made for the production of the new material with respect to the conventional process. This includes the different raw materials that are required for the production, the adjustments to the production process and the collection and recycling of used rubber products. First of all, the gum rubber that is used as a starting material for the production of the thermoreversibly cross-linked rubber compounds described in this thesis is a maleated ethylene/propylene rubber (EPM). The maleation step makes the EPM-g-MA gum rubber approximately 60% more expensive than the non-functionalized EP(D)M gum rubbers that are typically peroxide cured (approximately € 4,00 per kg for EPM-g-MA versus € 2,50 per kg for EPM). Since the gum rubber is the major contributor to

the price of the rubber compound (Figure 9.2), this will have the most significant influence on the cost price per batch. The addition of FFA or the use of BM instead of peroxide cross-linkers does not significantly contribute to the price of the final product. The proportion of the different components is derived from the compound formulation used in Chapter 8.



**Figure 9.2.** Pie charts showing the relative costs of the ingredients in A: peroxide cured EPM rubber compounds and B: thermoreversibly cross-linked EPM-g-MA rubber compounds with 140 phr carbon black and 50 phr oil.

The cost estimation for the production of the conventional, peroxide cured EPM and the thermoreversibly cross-linked EPM-g-furan rubber are both based on a primary rubber compound, i.e. produced from purely new materials (Table 9.2). Peroxide curing is assumed to require 5 phr of pure di(tert-butylperoxyisopropyl)benzene and 1 phr of coagent to achieve the same level of cross-linking and similar material properties. The 1,1-(Methylenedi-4,1-phenylene) bismaleimide cross-linker was chosen as a coagent as it happens to be one of the most frequently used coagent for the peroxide curing of elastomer [2,3]. The price of furfurylamine is an estimation based on the prospect of eventual large scale production and bio-sourcing.

**Table 9.2.** Cost estimations for the components required for the production of a batch of 600 kg of conventional, peroxide cured EPM and BM cross-linked EPM-g-furan rubber compound.

Component	Price (€/kg)	Peroxide cured compound		BM cross-linked compound	
		Amount (phr)	Costs (€/kg compound)	Amount (kg)	Costs (€/kg compound)
EPM	2.50	100	0.85	0	0
EPM-g-MA	4.00	0	0	100	1.37
Carbon black	1.00	140	0.47	140	0.47
Oil	0.75	50	0.13	50	0.13
Furfurylamine	2.00	0	0	1.5	0.01
Peroxide	6.00	5	0.10	0	0
Bismaleimide	15.00	1	0.05	1	0.05
<b>Total</b>		<b>296</b>	<b>1.60</b>	<b>293</b>	<b>2.03</b>

The 25% increase in costs of raw materials required for the production of the thermoreversibly cross-linked rubber compound with respect to the peroxide cured rubber compound should be overcome by the recycling of the reprocessable rubber to make the production economically feasible. Part of the higher costs of the starting

materials are accounted for by the possibility of reprocessing any scrap material that is usually lost during the production process (roughly 10%). In chapter 8 it was shown that the thermoreversibly cross-linked rubber can be reprocessed at least twice without any significant loss of material properties. Reprocessing used product twice instead of using new raw materials will lower the production costs as the costs of acquiring used products is only based on the costs of collecting them. The processing cost (mixing and vulcanization) for the production and the recycling of the reprocessable rubber compounds are assumed to be equal with equal processing times and without the use of any extra equipment.

It is crucial that the products are separated from non-reprocessable rubbers by discarding them in designated containers. The most cost-efficient way of collecting the recyclables is by gathering these containers directly at the production plant [4]. This enables total control over the acquisition of the recyclable products and is able to direct the amount of reprocessable rubber stock present in the processing plant. An estimation of the accommodated acquisition costs is based on the use of containers of approximately 1 m<sup>3</sup> with an average fill rate of 60%. The total acquisition costs of the recyclable rubber products is estimated to be €0.50 per kg based on a container size of 600 kg, an average distance between the collection containers and the production and recycling plant of 300 km, a fuel consumption of 15 L per 100 km and a factor to correct for the depreciation of distribution materials, man-hours (logistics and the removal of possible pollution) etc. The collected recyclable rubber products can be reprocessed by heating them to above 150 °C in an internal mixer. This recycling step can be performed on existing rubber production plants using the present equipment. The reprocessable rubber products however, have to be marked with a code (batch number) that gives information about their origin and how often the material has been reprocessed to minimize deterioration of material properties. Although only the material properties of fully recycled rubber products have been studied (Chapter 8), mixing new and used reprocessable rubber material could further improve the quality and reprocessability of the resulting products [5]. The material costs were estimated to be approximately €1.60 per kg for production of the conventional peroxide cured EPM and €2.03 per kg for the reprocessable, BM cross-linked EPM-g-furan. If all reprocessable material is recycled twice and the costs for reprocessing are equal to the normal processing costs, only the acquisition costs remain. This means that the production of three batches of the new, reprocessable rubber would cost roughly €3.03 per kg. The lower average costs of producing this reprocessable rubber compound (roughly €1,- per kg) with respect to conventional, peroxide cured rubber compounds (roughly €1,60 per kg) should compensate for the investments required to make the slight changes to the production process discussed (*vide supra*). As stated above, this case study is intended as a preliminary analysis of the factors that are required for an economic evaluation. As such, it does not take into account possible modification of the base formulation recipes (i.e. changes in the amount and kind of

additives such as fillers) nor the corresponding product properties and their possible optimization as the thermoreversible cross-links in this material were found to be in a constant dynamic equilibrium between their open and closed states at every temperature (Chapter 5). These aspects are briefly discussed in the following because the conditions at which this material can be applied have to be investigated before using the material in a product.

### 9.3. Experimental

#### 9.3.1. Materials

Non-cross-linked, peroxide cured and sulphur vulcanized EPDM reference samples with a medium ethylidene (ENB-EPDM, *Keltan 8550C*, 53 wt% ethylene, 5.5 wt% ENB) and non-cross-linked, maleated EPM (EPM-g-MA, *Keltan DE5005*, 49 wt% ethylene, 2.1 wt% MA,  $M_n = 50$  kg/mol, PDI = 2.0) were kindly provided by ARLANXEO Netherlands B.V. Prior to the reaction, EPM-g-MA was dried in a vacuum oven for one hour at 175 °C to convert present diacids into anhydride. Short cut aramid fibers (2 mm) were kindly provided by Teijin Aramid. Furfurylamine (FFA, Sigma-Aldrich, ≥99%) and 2-thiophenemethylamine (2-TMA, Sigma-Aldrich, 97%) were freshly distilled before use. 3-Cloropropylamine (APCl, > 99%), lithium cyclopentadiene (LiCp, > 99%), 1,1-(Methylenedi-4,1-phenylene)bismaleimide (BM, 95%), Multi walled carbon nanotubes (CNTs, O.D.×L = 6-9 nm × 5 μm, > 95%), Bis(t-butylperoxy-i-propyl) benzene (*Perkadox14-40*, AkzoNobel), Octadecyl-1-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate (99%), tetrahydrofuran (THF, >99.9%), decalin (98%) and acetone (>99.5%) were all bought from Sigma-Aldrich.

#### 9.3.2. Methods

##### 9.3.2.1. Furan-functionalization and BM cross-linking of EPM-g-MA

The EPM-g-MA precursor was converted into EPM-g-furan according to a reported procedure [6]. 40.0 g of EPM-g-furan (8.6 mmol furan content) and 40 mg anti-oxidant were dissolved in 500 mL THF. 0.5 eq. (based on furan content of EPM-g-furan as determined from characterization by infrared spectroscopy and elemental analysis) of the BM was dissolved in THF and added to the 10 wt% rubber solution under stirring. The majority of the solvent was evaporated in the fume hood by blowing over air. The residual solvent was removed in a vacuum oven at 50 °C and the resulting product was compression molded at 150 °C and 100 bar for 1 h and thermally annealed in an oven at 50 °C for 7 days. Compression molding was performed on a Taunus Ton Technik V8UP150A press, equipped with a temperature controller.

##### 9.3.2.2. Cyclopentadiene modification and cross-linking

45.0 g EPM-g-MA rubber (9.6 mmol MA) was dissolved in 500 mL THF at room temperature. 4.5 g of APCl (28.9 mmol; 3.0 eq. based on MA content in EPM-g-MA) was then added to the 10 wt% rubber solution. The reaction mixture was stirred for 5



h in a closed system at room temperature and then precipitated by pouring it slowly into a tenfold amount of acetone (5 L) under mechanical stirring, yielding the polymer product as white threads. The product (EPM-g-Cl) was dried to constant weight in an oven at 35 °C. Subsequently, the product was briefly compression molded at 175 °C and 100 bar to ensure the conversion of all intermediate maleimide acid products to imide products. 40.0 g of the resulting EPM-g-Cl (8.6 mmol pendant Cl groups as determined from characterization by infrared spectroscopy and elemental analysis) and 40 mg anti-oxidant were dissolved in 500 mL THF under N<sub>2</sub>. An equimolar amount of LiCp was added under stirring and left to react at 30 °C for 18 h. Afterwards, the reaction mixture was precipitated in a 20:1 molar excess of demi-water under mechanical stirring, yielding the polymer product as white threads. The product (EPM-g-Cp) was dried in a vacuum oven at 150 °C overnight to remove any traces of water and unreacted LiCp. The resulting product was compression molded at 150 °C and 100 bar for 1 h and thermally annealed in an oven at 90 °C for 3 days.

#### *9.3.2.3. Thiophene-functionalization and BM cross-linking of EPM-g-MA*

45.0 g EPM-g-MA rubber (9.6 mmol MA) was dissolved in 500 mL THF at room temperature. 3.2 g of freshly distilled 2-TMA (28.9 mmol; 3.0 eq. based on MA content in EPM-g-MA) was then added to the 10 wt% rubber solution. The reaction mixture was stirred for 5 h in a closed system at room temperature and then precipitated by pouring it slowly into a tenfold amount of acetone (5 L) under mechanical stirring, yielding the polymer product as white threads. The product (EPM-g-thiophene) was dried to constant weight in an oven at 35 °C. Subsequently, the product was briefly compression molded at 175 °C and 100 bar to ensure the conversion of all intermediate maleimide acid products to imide products. 40.0 g of the resulting EPM-g-thiophene (8.6 mmol thiophene content as determined from characterization by infrared spectroscopy and elemental analysis) and 40 mg anti-oxidant were dissolved in 500 mL THF. 0.5 eq. (based on thiophene content of EPM-g-thiophene) of the BM was dissolved in THF and added to the 10 wt% rubber solution under stirring. The majority of the solvent was evaporated in the fume hood by blowing over air. The residual solvent was removed in a vacuum oven at 50 °C and the resulting product was compression molded at 150 °C and 100 bar for 1 h and thermally annealed in an oven at 90 °C for 3 days.

#### *9.3.2.4. Preparation of CNT-filled, BM cross-linked EPM-g-furan rubber compounds*

First, 0.22 g of CNTs was dispersed in 50 mL THF by sonication for 15 min. Subsequently, 0.020 g BM was dissolved in 10 mL THF and mixed with the dispersed CNTs. The mixture was refluxed at 50 °C for 1 day. Hereafter, the dispersion was filtered and washed. The residue was dried in an oven at 50 °C until constant weight was reached. The resulting CNT/BM mixture was suspended in 50 mL THF by sonication for 30 min. Then, 5 g of EPM-g-MA or EPM-g-furan was dissolved in 50 mL THF, mixed with the suspended filler and stirred for 15 min. The resulting mixture

was sonicated for 30 min and refluxed at 50 °C for 24 h. The majority of the solvent was evaporated in the fume hood by blowing over air. The residual solvent was removed in a vacuum oven at 50 °C. The resulting product was compression molded at 150 °C and 100 bar for 15 min and thermally annealed in an oven at 50 °C for 3 days.

#### 9.3.2.5. *Preparation of fiber-filled, BM cross-linked EPM-g-furan rubber compounds*

18 g of EPM-g-furan was fed to an internal mixer (70% fill factor) and homogenized at 50 rpm and 130 °C for 4 min. Then, 1, 3 or 5 phr of short cut aramid fibers was added. When the torque was stable (after typically 2-3 min), the BM cross-linker was added (0.2 to 1.5 molar eq. based on furan content). Mixing was continued for 2 min before the compound was removed from the mixer. Sample bars of the obtained products were obtained by pre-heating the materials in a mold at 140 °C for 5 min and compression molding them at 140 °C and 100 bars for 15 min. The resulting sample bars were thermally annealed in an oven at 50°C for a minimum of 72 h to ensure complete cross-linking.

#### 9.3.2.6. *Preparation of fiber-filled, peroxide cured ENB-EPDM rubber compounds*

18 g of ENB-EPDM was fed to an internal mixer (70% fill factor) and homogenized at 50 rpm and 70 °C for 4 min. Then, 1, 3 or 5 phr of short cut aramid fibers was added. When the torque was stable (after typically 2-3 min), 0.5, 1 or 2 phr of pure peroxide was added slowly to the mixture. The rubber compound was mixed for 4 more min until it was removed from the mixer. This rubber compound was then vulcanized by pre-heating in a mold at 160 °C for 5 min and compression molding at 160 °C and 50 bars for 35 min.

### 9.3.3. *Characterization*

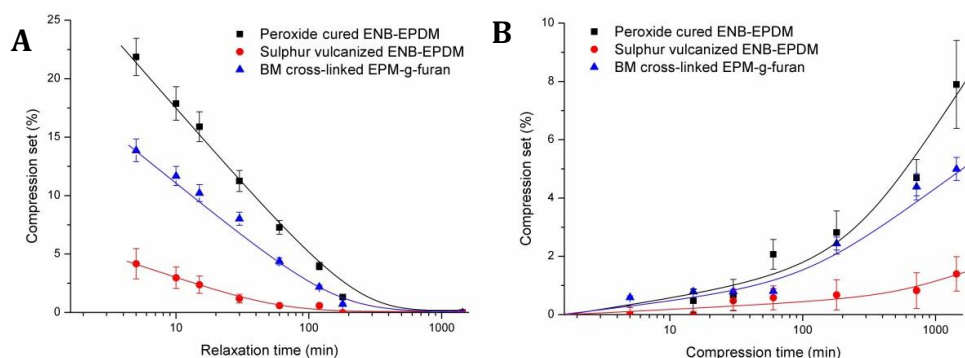
The conversion of EPM-g-MA to EPM-g-furan, EPM-g-thiophene and EPM-g-Cl was followed by Fourier Transform Infrared spectroscopy (FT-IR) and elemental analysis (EA). FT-IR spectra were recorded on a Perkin-Elmer Spectrum 2000. Rubber films with a thickness of 0.1 mm were compression molded at 150 °C and 100 bar for 30 min, thermally annealed to ensure maximum DA cross-linking and measured in a KBr tablet holder. Measurements were performed over a spectral range from 4000 to 600  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ , co-averaging 32 scans. Deconvolution was used to quantify the areas under the individual FT-IR peaks ( $R^2 > 0.95$ ). The differences in relative peak areas were used to calculate the reaction conversions. The methyl rocking vibration peak at 723  $\text{cm}^{-1}$  was used as an internal reference, as it originates from the EPM backbone and is not affected by chemical modification. The decrease of the absorbance of the C=O symmetrical stretch vibration of the anhydride groups at 1856  $\text{cm}^{-1}$  was used to calculate the conversion of the reaction from EPM-g-MA to EPM-g-furan, according to a reported procedure [6]. EA for the elements N, C and H was performed on a Euro EA elemental analyzer. The nitrogen content was related to the anhydride conversion according to a reported procedure [6].

Tensile tests were performed on an Instron 5565 with a clamp length of 15 mm, according to the ASTM D4-112 standard. A strain rate of  $500 \pm 50$  mm/min was applied. Test samples of 45 mm long, 5 mm wide and 1 mm thick were prepared by compression molding. For each measurement 10 samples were tested and the two outliers with the highest and the lowest values were excluded. Data presented are averages of the other 8 tests. The median stress-strain curves in the figures were selected to represent the entire series of a sample. Compression set tests were generally performed according to the ASTM D931 standard, using a home-made device and cylindrical samples with a thickness of  $6.0 \pm 0.1$  mm and a diameter of  $13.0 \pm 0.1$  mm, which were prepared by compression molding. The samples were compressed to 75% of their original thickness for 70 h at room temperature and relaxed for 30 min at 50 °C. Another series of compression set experiments was performed in which the samples were compressed to 75% of their original thickness for 70 h at 25, 60, 100 and 140 °C and relaxed for 30 min at room temperature. The Joule effect was visualized by exposing a sample bar of  $\pm 2.5$  cm to a potential source and measuring the applied current and the drop in voltage. At steady state heat generation, thermographic images were collected with a Fluke Ti10 IR Fusion Technology camera. Conductive self-healing was performed in the same set-up using a sample that was cut in half. The fresh cross-sections were fused together by exposing the connected sample bar ends to a potential source for 90 min.

## 9.4. Results and discussion

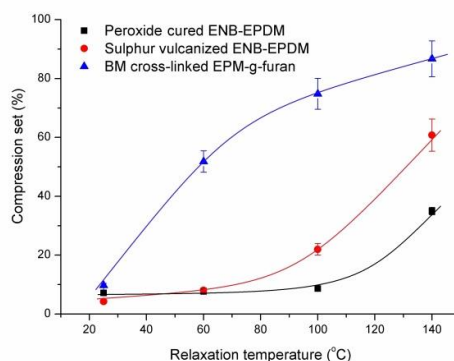
### 9.4.1. Application window

The furan-functionalization and BM cross-linking of EPM-g-MA was successfully performed and analyzed according to a reported procedure [6]. The cross-link density of the thermoreversibly cross-linked rubber product was found to be  $2.07 \cdot 10^{-4} \pm 0.21 \cdot 10^{-4}$  mol/mL, which is similar to that of the peroxide cured and sulphur vulcanized EPDM reference samples ( $1.98 \cdot 10^{-4} \pm 0.18 \cdot 10^{-4}$  and  $1.85 \cdot 10^{-4} \pm 0.16 \cdot 10^{-4}$  mol/mL, respectively). The stability or creep behavior of the samples is examined by performing compression set experiments under different conditions (Figure 9.3). A comparison with measurements on peroxide cured and sulphur vulcanized EPDM rubbers was used to investigate how the dynamic equilibrium of the thermoreversible cross-links affects the material properties at room temperature. The relaxation time of different characteristic gum rubbers was followed after 70 h of compression (Figure 9.3A) and different compression times were followed by 30 min relaxation at room temperature (Figure 9.3B).



**Figure 9.3.** Compression set tests of BM cross-linked EPM-g-furan samples and of peroxide cured and sulphur vulcanized EPDM reference samples with similar cross-link densities applying A: different relaxation times after 70 h of compression and B: 30 min relaxation after different compression times at room temperature. The lines are for illustrative purposes only. Error bars indicate  $\pm 1$  standard deviation.

The relaxation time of the BM cross-linked EPM-g-furan required to reach the desired compression set value is in between that of the sulfur vulcanized and peroxide cured EPDM reference samples with similar cross-link densities. Similarly, the influence of longer compression times on these thermoreversibly cross-linked samples is also in between that of the two reference samples. It can therefore be concluded that the dynamic character of the thermoreversible cross-links does not have a significant effect on the elastic properties of the reprocessable rubbers at room temperature. The compression set of BM cross-linked EPM-g-furan and the peroxide cured and sulphur vulcanized EPDM reference samples has also been measured at different temperatures (Figure 9.4).



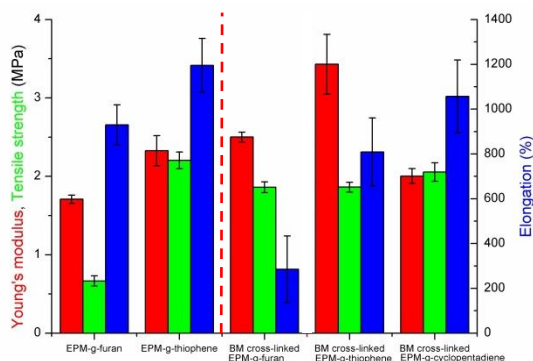
**Figure 9.4.** Compression set at different temperatures of BM cross-linked EPM-g-furan samples and of peroxide cured and sulphur vulcanized EPDM reference samples with similar cross-link densities. The lines are for illustrative purposes only. The error bars indicate  $\pm 1$  standard deviation.

Although the room temperature compression set is similar for all samples, it appears that a slight increase in temperature has a detrimental effect on the compression set of the thermoreversibly cross-linked EPM-g-furan samples with respect to the irreversibly cross-linked reference samples. This may be due to a shift in the DA reaction equilibrium towards the retro-DA reaction at elevated temperatures. The dynamic equilibrium may allow for a rearrangement of the cross-links to accommodate a certain degree of imposed compression. This means that the use of these reprocessable rubbers is strictly limited to room temperature applications such as wire and cable insulation or sealant applications. An additional limitation to the use of the DA chemistry for the thermoreversible cross-linking of elastomers is the aromatization of the DA adduct by the elimination of water. This side-reaction becomes predominant at temperatures above 200 °C due to high energy consumption of the reaction mechanism [7]. Even so, repeated reprocessing at high temperatures may lead to the occurrence of a certain degree of this irreversible side-reaction and a subsequent deterioration of reprocessability. There are several solutions and alternatives to overcome this and the sensibility of the material to slight increases in temperature.

### **3.2. *Alternatives yielding improved high temperature performance***

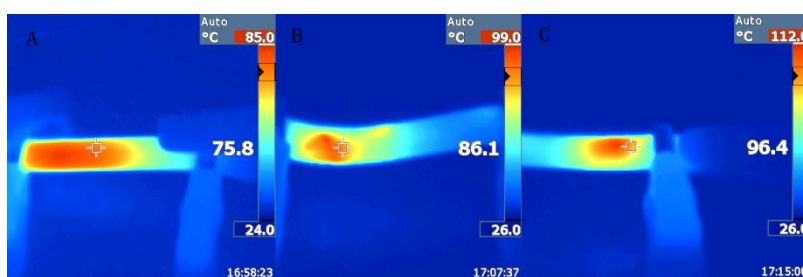
Other diene-dienophile couples can be used to thermoreversibly cross-link the modified elastomers via DA chemistry [8]. Especially cyclopentadiene seems to be a good alternative for the furan-maleimide couple as the temperature at which the retro-DA reaction becomes prevalent is higher (150-215 °C for cyclopentadiene [9,10] versus 110-170 °C for furan-maleimide [11-13]). Some preliminary experiments were performed in which EPM-g-MA was functionalized with 3-chloropropylamine and the resulting pendant chloride group was reacted with lithium cyclopentadiene [14]. Although this approach seemed to be successful for the highly functionalized polyketones used in a previously reported procedure [14], the application to EPM-g-MA elastomers with a low degree of functionalization was less successful. The high reactivity of the cyclopentadiene groups is responsible for a number of side-reactions [15], resulting in a low conversion. More importantly, the formation of cross-links between pendant cyclopentadienes was found to proceed much slower for this system with respect to the furan-bismaleimide couple. This may be due to the lower concentration of functional groups, but is also likely to be a result of the low mobility of the polymer backbones that make it hard for the functional groups to recombine. The relatively small, bifunctional BM cross-linking agents were found to have a relatively high mobility in the rubber matrix, allowing for a faster recombination of diene and dienophile. As a result, the cyclopentadiene cross-linked EPM has a lower Young's modulus and higher elongation at break with than the BM cross-linked EPM-g-furan (Figure 9.5). Another preliminary experiment was executed in which EPM-g-MA was modified with 2-thiophenemethylamine and the resulting EPM-g-thiophene was cross-linked with BM. The resulting material was cross-linked based on its

insolubility and the high Young's modulus and low elongation at break with respect to its non-cross-linked precursor (Figure 9.5). Nevertheless, even though the retro-DA reaction may only become prevalent at higher temperatures for this diene-dienophile couple, this would also imply that the aromatization side-reaction becomes more prevalent.



**Figure 9.5.** Tensile test results of non-cross-linked EPM-g-furan and EPM-g-thiophene, their BM cross-linked products and a cyclopentadiene cross-linked EPM gum rubber. Error bars indicate  $\pm 1$  standard deviation.

Alternatives to overcome problems related to using DA chemistry as a tool to thermoreversibly cross-link elastomers could involve the use of other external stimuli to control the reversibility of the cross-links [17]. Preliminary experiments in using conductivity as an external stimulus for the reversible cross-linking of carbon nanotube (CNT) filled, BM cross-linked EPM-g-furan rubbers showed that the Joule effect results in heating up of the samples and indeed facilitates the conductive self-healing of the material (Figure 9.6).



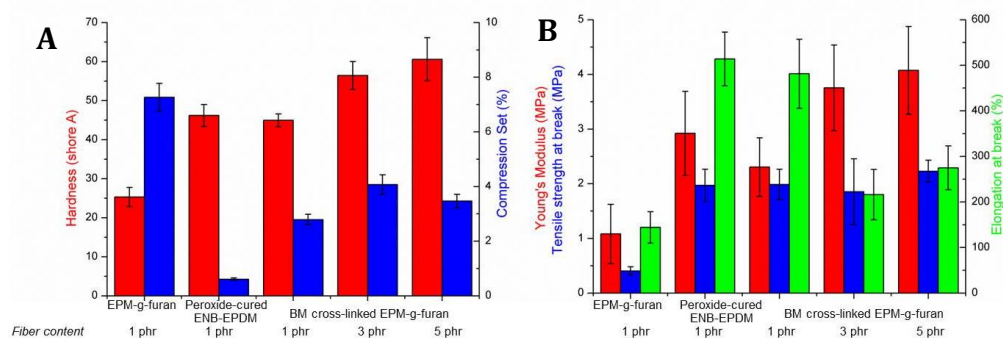
**Figure 9.6** Thermal images of A: EPM-g-MA ( $I = 0.062$  A), B: non-cross-linked EPM-g-furan ( $I = 0.024$  A) and C: BM cross-linked EPM-g-furan ( $I = 0.049$  A) all with 10 wt% carbon nanotubes. The color indicates of the bar an increase in temperature going from blue to red as indicated by the legend.

Other external stimuli that could be considered for thermoreversible cross-linking are magnetism, pH or light [18-21]. Carbene insertions for example could be considered for the modification of the rubber as the resulting compounds induce a certain amount

of photo cross-linking [22]. However, the main advantage of using temperature as an external stimulus is that the rubber production process would not have to be adapted in order to facilitate the reprocessing of the thermoreversibly cross-linked rubber products. Using another external stimulus for reprocessing the rubber products would imply a significant adaptation of the process.

#### 9.4.2. Product Application

Finally, rubber products are usually reinforced with fillers such as aramid fibers. For the BM cross-linked EPM-g-furan, the Hardness and Young's modulus increase and the elongation at break of the rubber compounds decreases upon compounding with larger amounts of short cut aramid fiber (Figure 9.7). No significant changes were observed in the tensile strength and the compression set. With the exception of the compression set, the effect of fiber loading of the thermoreversibly cross-linked rubbers on the material properties was the same as for fiber-loaded, peroxide cured ENB-EPMD rubbers with the same cross-link density ( $2.45 \cdot 10^{-4} \pm 0.28 \cdot 10^{-4}$  and  $2.63 \cdot 10^{-4} \pm 0.27 \cdot 10^{-4}$ , respectively). The inferior compression set of the thermoreversibly cross-linked rubbers with respect to that of the peroxide cured reference sample may be a result of the rearrangement of cross-links under compression. Nevertheless, fiber filled rubber products may prove to be a suitable application for thermoreversibly cross-linked rubber.



**Figure 9.7.** A: Hardness and compression set at room temperature and B: Young's modulus, tensile strength and elongation at break of non-cross-linked EPM-g-furan and peroxide cured ENB EPDM with 1 phr of short cut aramid fibers and BM cross-linked EPM-g-furan with different fiber loading. Error bars indicate  $\pm 1$  standard deviation.

## 9.6. Conclusions

A technical assessment of the production, recycling and implementation in products of the thermoreversibly cross-linked rubber compounds described in this thesis was performed. The process required for the production of conventional, peroxide cured EPM and the new, reprocessable rubber compounds was compared for a batch mixer process and studied for a business to business scenario. The current production process does not have to be significantly adapted to facilitate the production and recycling of these new, reprocessable rubber compounds. Furthermore, the higher costs of the raw materials required for their production are more than compensated for by recycling the products twice. Including the acquisition costs of roughly € 0.50 per kg for collecting all used, reprocessable rubber products, the price of the production and twice recycling of the new, reprocessable rubber is estimated to be € 1,- per kg. This is 33% lower than the estimated € 1,50 per kg for the production of conventional, peroxide cured EPM compounds.

The applicability of a newly developed, reprocessable EPM rubber was studied by determining the material properties under different conditions. Although the dynamic character of the thermoreversible cross-links does not have a significant effect on the elastic properties of the reprocessable rubbers at room temperature, the application of these thermoreversibly cross-linked elastomers remain limited to room temperature applications due to the rapid deterioration of the material properties upon a slight increase in temperature with respect to irreversibly cross-linked rubbers. As the material properties are stable at lower temperatures, it could be used in products for cable and wire insulation or sealing applications. Using alternative diene-dienophile couples such as cyclopentadiene or thiophene for the DA cross-linking reactions are proposed to overcome issues regarding the temperature stability of the reprocessable rubber compounds. Using such components should increase the threshold temperature for the retro-DA de-cross-linking reaction. A disadvantage of this approach is the aromatization of the Diels-Alder adduct that is a side-reaction which is also more prevalent at higher temperatures. Using other external stimuli such as electricity, magnetism, pH or light for the control of the cross-linking process is proposed. Although this would help overcome the issues related to temperature stability, this would also imply that the reprocessing of the material would require a significant adaptation of the current rubber production process. Finally, the BM cross-linked EPM-g-furan rubber was used for the preparation of aramid fiber reinforced rubbers. The material properties of the resulting products are comparable to that of the fiber reinforced, peroxide cured reference sample and improve with the fiber loading.



## 9.7. References

- [1] Borzenski F. *Continuous Mixing of Polymeric Compounds*. Lippincott & Peto, Inc., Connecticut **1998**.
- [2] van Duin M. *Kaut Gummi Kunst* **2002**;55:150.
- [3] Dikland HG. *Coagents in Peroxide Vulcanizations of EP(D)M Rubber*, PhD thesis University of Twente **1992**.
- [4] Schlesinger ME. *Aluminium Recycling*. CRC Press, Boca Raton **2006**.
- [5] Herder C, Picchioni F. *ICRM2014*, Kottayam, India, April 12, **2014**.
- [6] Polgar LM, van Duin M, Picchioni F. *J. Vis. Exp.* **2016**;e54496.
- [7] Polgar LM, Kingma A, Roelfs M, van Essen M, van Duin M, Picchioni F. *Kinetics of cross-linking and de-cross-linking of EPM rubber with thermoreversible Diels-Alder chemistry. Provisionally accepted for publication in Eur Polym J* **2016**
- [8] Patet RE, Nikbin N, Williams CL, Green SK, Chang C, Fan W, Caratzoulas S, Dauenhauer PJ, Vlachos DG. *Acs Catal* **2015**;5:2367.
- [9] Toncelli C, de Reus D, Broekhuis AA, Picchioni F. Thermoreversibility in Polymeric Systems. In: *Self-Healing at the Nanoscale*: Amendol V, Meneghetti M Eds. CRC Press, Boca Raton **2011**.
- [10] Peterson AM, Palmese GR. *Click Chemistry for Biotechnology and Materials Science*. Wiley, Hoboken **2009**.
- [11] Stille J, Plummer L. *J Org Chem* **1961**;26:4026.
- [12] Chen XX, Dam MA, Ono K, Mal A, Shen HB, Nutt SR, Sheran K, Wudl F. *Science* **2002**;295:1698.
- [13] Teramoto N, Arai Y, Shibata M. *Carbohydr Polym* **2006**;64:78.
- [14] Gandini A, Coelho D, Silvestre AJD. *Eur Polym J* **2008**;44:4029.
- [15] Toncelli C, Bouwhuis S, Broekhuis AA, Picchioni F. *J Appl Polym Sci* **2016**;133:42924.
- [16] Kobuke Y, Fueno T, Furukawa J. *J Am Chem Soc* **1970**;92:6548.
- [17] Imbernon L, Norvez S. *Eur Polym J* **2016**;82:347.
- [18] van der Zwaag S. *Self-Healing Materials*. Springer, New York **2007**.
- [19] Leng J, Lan X, Liu Y, Du S. *Prog Mater Sci* **2011**;56:1077.
- [20] Murphy EB, Wudl F. *Prog Polym Sci* **2010**;35:223.
- [21] Meng H, Li G. *Polymer* **2013**;54:2199.
- [22] Blencowe A, Blencowe C, Cosstick K, Hayes W. *React Funct Polym* **2008**;68:868.